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Trends in the bulk deposition and atmospheric concentration of air pollutants in the Finnish Integrated Monitoring catchment Pallas during 1992–2012

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The air and precipitation chemistry of 15 components was monitored within the Pallas Integrated Monitoring catchment during 1992–2012. A continuous time series of 21 years was available for the bulk deposition of acidifying compounds and base cations, whereas for the atmospheric concentration of sulphur and nitrogen compounds and ozone, the measurements covered 14–21 years. In this paper, an updated analysis of trends in these time series is presented and discussed in relation to the development in European emissions. The most notable result, a significant increase in NO_3 bulk deposition since 1997, could serve as a general warning of the threats of excessive nutrient inputs to the vulnerable arctic ecosystems. There were no major changes in ozone concentrations between 1992–2012. The annually averaged source areas of gaseous SO_2 and NO_2 detected at Pallas were estimated using air parcel back trajectories.

Introduction

Increased emissions of air pollutants have caused severe environmental problems at local, regional and global scales (Rohde *et al*. 1995, Galloway *et al*. 2004). Since the 1980s, environmental regulations negotiated under the Convention on Long-Range Transboundary Air Pollution (CLRTAP) have led to decreased emissions of key air pollutants in Europe. The Integrated Monitoring (IM) Programme is one of the five International Co-operative Programmes carried out under the CLRTAP. The aim of the programme is to investigate the influence of transboundary atmospheric deposition on natural ecosystems (Bull *et al*. 2001). Extensive monitoring of atmospheric concentrations and deposition is essential for the successful fulfilment of the IM programme.

Results from the first five (Bergström *et al*. 1995) and ten years (Ruoho-Airola *et al*. 1998) of atmospheric deposition monitoring at the Finnish IM stations have been published earlier. The main results of the two other presently active Finnish IM stations, Valkea-Kotinen and Hietajärvi, have been compiled in a special issue of *Boreal Environment Research* (e.g. Rask *et al*. 2014, Ruoho-Airola *et al*. 2014) and in a report (Niinioja and Rämö 2006).

Measurements of the atmospheric load at Pallas now cover 21 years for acidifying compounds and up to 17 years for gaseous com-

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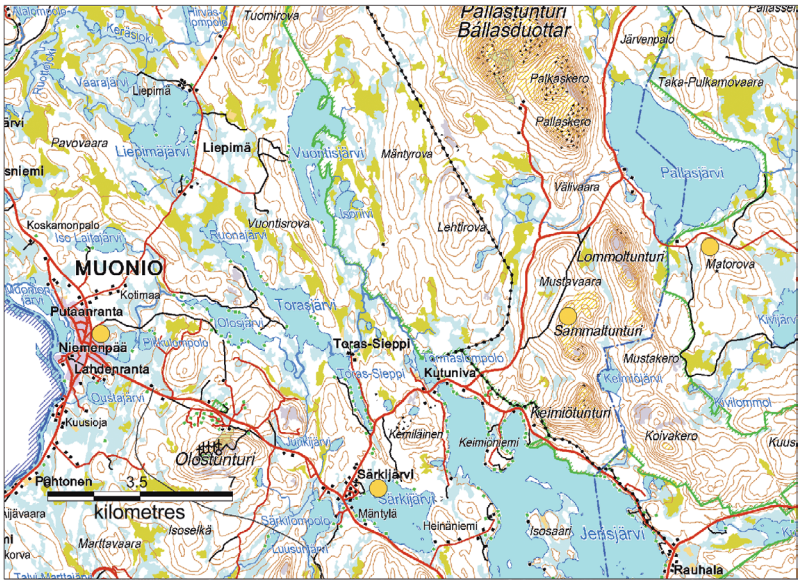

Fig. 1. Map of the Pallas station area. The measurement sites and the Alamuonio meteorological station are indicated by yellow circles. Map ©National Land Survey of Finland, Topographic Database 10/2014 [terms of use at http://www.maanmittauslaitos.fi/en/NLS_open_data_licence_version1_20120501].

pounds. This homogeneous and continuous set of high-quality data has enabled us to update existing knowledge on the levels of and trends in atmospheric pollution in the subarctic part of Finland.

This paper aims to present atmospheric bulk depositions of the main ions affecting acidification and eutrophication, as well as gaseous compounds measured at Pallas, and to provide an overview of concentration and deposition trends over the measurement period. The importance of different source areas for the SO_2 and NO_2 concentrations detected at Pallas is examined with air mass back trajectories. The results are expected to reflect the changes in European emissions. In particular, NO_3 deposition is discussed because of the risk of increased nutrient inputs to the vulnerable arctic ecosystems. The atmospheric trends in the Pallas area are also of general interest, as environmental changes due to climate change are expected to take place earlier and to be stronger in the Arctic.

Material and methods

Site and measurements

The Finnish Meteorological Institute's Pallas station is located in the subarctic region at the northernmost limit of the northern boreal forest zone. Pallas represents well the continental background air of the subarctic region (Hatakka *et al*. 2003). In the Pallas area, there are several measurement sites within about 20 km from each other (Fig. 1). The precipitation chemistry samples were first collected at the Särkijärvi site (67°55´N, 23°55´E, 260 m a.s.l.), which was operational from 1991 to 1999. Precipitation chemistry sampling was moved to the Matorova site (68°00´N, 24°14´E, 340 m a.s.l.), 16 km to the east-northeast of the Särkijärvi site, in January 2000. Filter sampling for the concentration of gaseous and particulate sulphur and nitrogen compounds in air was also carried out at the Matorova site. The results for the continuous monitoring of the gaseous compounds are from the Sammaltunturi site (67°58´N, 24°07´E, 565 m a.s.l.). The Särkijärvi site is situated within the restricted area of the border guard, in a flat opening surrounded by coniferous forest and a lake 500 m to the south (Vuorenmaa *et al*. 2001). Matorova lies six kilometres east-northeast of Sammaltunturi and is situated on the top of a hill covered by coniferous forest in the middle of a one-hectare clearing. The Sammaltunturi station resides on top of a fjeld at an elevation of 565 m a.s.l. The vegetation on the fjeld top is sparse, mainly consisting of low vascular plants, moss and lichen (Hatakka *et al*. 2003).

The cooperation within the ICP Integrated Monitoring programme at the Pallas station started in 2005. Before then, data from the Pallas station had been collected within the WMO GAW and LRTAP EMEP programmes. Table 1 lists the content of the different Integrated Monitoring subprogrammes covered in this study. The precipitation chemistry subprogramme has continued since 1 November 1991. Initially, the measurement programme covered the main anions and cations in precipitation that have an impact on atmospheric acidification and the eutrophication of ecosystems. Later, air chemistry monitoring was added to the programme. Measurements at the meteorological stations near the Pallas station cover the whole monitoring period.

The research at the Pallas sites is introduced in detail in the overview article by Hatakka *et al*. (2003), to which the reader is referred for further information on the sites and methods.

Sampling and analysis of the precipitation and air chemistry programmes

The methods recommended in the EMEP Programme (EMEP 2001) were used. NILU-type bulk samplers (polyethylene) with an opening of 200 mm were used for the sampling of precipitation. The sampling height was about 1.6 m. Because the samplers were always open, part of the dry deposition was included in the samples. The weekly samples were combined after visual checking to give monthly samples. The deposition was calculated using the actual rainfall amount collected by the bulk sampler.

The filter pack samples for air chemistry at the Matorova site were collected using an open-face filter pack with an NaOH-impregnated Whatman 40 filter. The sampling height was about 3 m. Particulate SO_4 was sampled on a Whatman 40 filter installed in front of an SO_2 sampling unit. The sum of the gaseous HNO_3 and particulate NO_3 were sampled using the same filter pack as the sulphur compounds. For the sum of the gaseous NH_3 and particulate NH_4, a second filter line was used with a $(COOH)_2$-impregnated Whatman 40 filter. After the beginning of 2007, all the

Table 1. Precipitation, air quality and meteorological measurements in the Pallas Integrated Monitoring area.

IM Subprogramme	Site	Frequency of sampling	Components measured	Start of sampling	End of sampling
Precipitation chemistry	Särkijärvi	1 week	H^+, Cl, NO_3, SO_4, NH_4, Mg, Ca, Na, K	1 Nov. 1991	31 Dec. 1999
Precipitation chemistry	Matorova	1 week	H^+, Cl, NO_3, SO_4, NH_4, Mg, Ca, Na, K	1 Jan. 2000	
Air chemistry, filter pack samples	Matorova	1 day	SO_2, SO_4, NH_3 + NH_4, HNO_3 + NO_3	1 Jan. 1996	change of method on 1 Jan. 2007
Air chemistry, continuous	Sammaltunturi	1 hour	SO_2, NO_2, O_3	1 Jan. 1995	
Meteorology	Alamuonio and Sammaltunturi	1–24 hours	Precipitation, temperature, humidity, wind velocity and direction, UV radiation	1 Mar. 1946	

filters were placed in one filter pack and the front filter was changed to a PTFE (Millipore 3 μm) filter. All anions and cations in the samples for precipitation and the filter packs were analysed by ion chromatography, the particles and gases after H_2O extraction at the Air Chemistry Laboratory of the Finnish Meteorological Institute (EN ISO/IEC 17025 accredited).

At the Sammaltunturi site, continuous measuring monitors were used to measure the air concentration of gases. O_3 was monitored by the UV photometric method, NO_2 by the chemiluminescence method and SO_2 by the UV fluorescence method. The sampling height was about 3 m. The monitoring methods are based on ISO or EN standards, and for all these measurements the calibration of the monitor is traceable to the SI unit or international primary standard through the Finnish national reference laboratory on air quality (http://www.finas.fi/Scopes/K043_A10_2013.pdf).

The results of the Air Chemistry Laboratory of the Finnish Meteorological Institute achieved good agreement with expected values in the intercalibrations of analytical methods arranged by the EMEP Chemical Coordinating Centre (CCC). In the precipitation samples, the deviation from the expected value was within 5% for the sulphur and nitrogen compounds and within 10% for other compounds. For the compounds in the filter pack samples, the deviation was within 15% (Uggerud and Hjellbrekke 2011). At the low concentrations typical for Pallas, the combined expanded measurement uncertainty for the components measured with the filter pack samples was between 0.010 μg m^{-3} for (HNO_3 + NO_3)-N and 0.045 μg m^{-3} for SO_2-S (Karlsson *et al*. 2007).

Trend calculation

Periods with a continuous change in the monthly time series were determined with the help of a Gaussian low pass filter (SD = two years). For the interpretation of climatological time series, the use of a low-pass filter has been recommended by the World Meteorological Organization (Mitchell *et al*. 1966). The weighting coefficients for this moving average are set to correspond to the ordinates of a Gaussian probability curve and give the ideal shape of a low pass filter for the visual inspection of possible systematic changes (Mitchell *et al*. 1966). The peak values thus gradually affect the average value without steep changes and the curve settles down, better showing the long-term trends. Climatologists often use the Gaussian filter method to display the low-frequency component in time series (*see* e.g. Patz *et al*. 2002, Lindström and Alexandersson 2004, Tuomenvirta 2004). The use of the Gaussian filter method for air quality time series is presented in Ruoho-Airola *et al*. (2006).

A generalized least-squares (GLS) regression with classical decomposition and autoregressive moving average (ARMA) errors used for monthly mean values was carried out using the method of Brockwell and Davies (2002) (ITSM Professional 7.3, B and D Enterprises Inc.). The detailed steps used for the calculation of the seasonal components by a moving average with a 13-month window, a preliminary regression model for the trend in the deseasonalized data, the iteration of the optimal ARMA(p,q) model for the residuals and the final estimates for the trend and error structure are described in Anttila and Tuovinen (2009). Further principles of the method are presented in Brockwell and Davies (2002).

Source analysis

The annually averaged source areas of gaseous SO_2-S and NO_2-N detected at Pallas between 2000 and 2010 were estimated using 120-hour air parcel back trajectories. Briefly, eight EMEP Flextra 120-h back trajectories (Pallas as the endpoint) per day for a height of 500 m above ground level were superimposed on a 1° × 1° geographical grid (Stohl *et al*. 1995, Stohl and Seibert 1998, Paatero and Hatakka 2000). The three-hourly mean concentration measured at Pallas was then attributed to all grid cells crossed by the appropriate trajectory. Finally, from all the realizations, the average concentration field for a particular cell was obtained by calculating the average of the concentration values for those hours when the connected trajectory hit this particular cell weighted by the time the trajectory

spent within the cell. The cell in which Pallas is situated therefore obtains a value close to the annual mean concentration measured at Pallas. A high concentration value in a grid cell means that, on average, air masses crossing over this cell result in high concentrations at the Pallas measurement site. Trajectory "heat maps", i.e. maps showing the total number of air mass trajectories crossing over each particular grid cell, were also produced. From these we can estimate the significance of the results; with an increasing distance from Pallas, fewer and fewer trajectories hit individual cells, reducing the accuracy of the information.

Results

Bulk deposition

The monitoring period for the main anions and cations in precipitation in the Pallas area covered 21 years. The annual bulk deposition levels of the components are examined for the beginning, middle and end of the period as three-year mean depositions for the periods 1992–1994, 2001–2003 and 2010–2012 (Table 2). This approach smooths the impact of short-term interannual variation.

For sulphate, chloride, sodium and potassium, the highest annual bulk deposition levels were detected at the beginning of the monitoring period. For all compounds except ammonium, calcium and magnesium, the annual levels decreased during the first half of the monitoring period. For nitrate, hydrogen ions and magnesium, the highest annual bulk deposition levels were measured at the end of the monitoring period, i.e., in 2010–2012.

The annual deposition levels strongly depended on weather conditions, including the amount of precipitation. The average annual precipitation for the same three-year periods, 1992–1994, 2001–2003 and 2010–2012, were 518, 544 and 570 mm, respectively. These were measured at Alamuonio, the nearest meteorological station to Pallas with data covering the whole monitoring period. The increase in the mean annual precipitation amount between the three-year periods was in both cases 5%.

The annual volume-weighted mean concentration of sulphate, nitrate and ammonium in precipitation behaved differently between 1992 and 2012 (Fig. 2A). On average, sulphate concentrations decreased, although not monotonously. The concentration of ammonium was also lower at the end of the period as compared with that at the beginning, although the peak values occurred in 1999 and 2002. In the annual nitrate concentration, some higher values were recorded during the first years of the monitoring, after which it remained between 0.10 and 0.15 mg N l^{-1}. However, the annual deposition of nitrate increased between 1997 and 2012 (Fig. 2B).

Air concentrations

The monitoring of the gaseous and particulate compounds in air started later than the monitoring of the precipitation samples (*see* Table 3; note that only two latter periods are the same as those in Table 2).

Both SO_2 and the particulate SO_4 concentration decreased from the beginning of the monitoring period until 2006. From 2007, in the new time series after the change in the sampling method, the decline continued until 2010, when the annual concentration peaked and remained at a slightly elevated level. The continuous time series of NO_2 first started in 2000. Higher annual mean values were measured in 2003–2005 and again in 2012.

Table 2. Mean annual bulk depositions of the main ions in precipitation at Pallas.

Period	SO_4-S (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	H^+ (μmol m^{-2})	Cl (mg m^{-2})	Na (mg m^{-2})	K (mg m^{-2})	Ca (mg m^{-2})	Mg (mg m^{-2})
1992–1994	114	64	40	7330	115	83	56	23	6
2001–2003	94	58	48	7270	69	45	15	34	8
2010–2012	99	79	43	9230	81	47	20	23	9

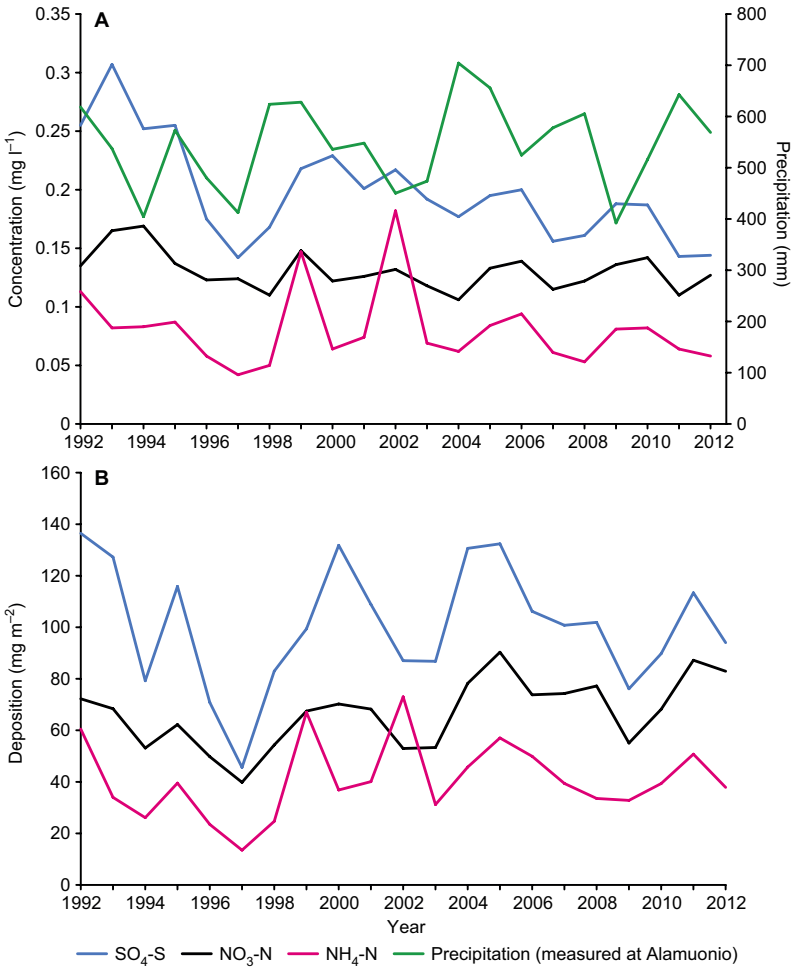

Fig. 2. Annual volume-weighted mean (**A**) concentration and (**B**) deposition of sulphate and the nitrogen compounds in precipitation.

The level of HNO_3 + NO_3 in air was much lower than the level of the primary component, NO_2, during the entire monitoring period, and no change in the levels of the oxidized products was detected. The levels of the ammonium components in air also remained relatively unchanged.

The ozone concentrations ($[O_3]$) measured at Pallas are presented here first as summary statistics for 1992–2012 (2010–2011 missing). The selected statistics show the annual variation in the mean and key percentiles that characterise the frequency distribution of $[O_3]$ for the summer half of the year (April–September) (Fig. 3). These months represent the period with the most intense ozone production and highest potential for detrimental effects of ozone on vegetation.

For about 20% of the time, $[O_3]$ was less than 50 μg m^{-3}, and the annual $[O_3]$ median

Table 3. Mean annual sulphur and nitrogen compound concentrations (μg m^{-3}) in air at Pallas. Note that the sampling method for SO_2, SO_4, HNO_3 + NO_3 and NH_3 + NH_4 changed in 2007 which caused a break in the time series.

Period	SO_2-S	SO_4-S	NO_2-N	(HNO_3 + NO_3)-N	(NH_3 + NH_4)-N
1996–1998	0.41	0.35	–	0.05	0.10
2004–2006	0.21	0.29	0.32	0.05	0.12
2010–2012	0.27	0.24	0.26	0.05	0.11

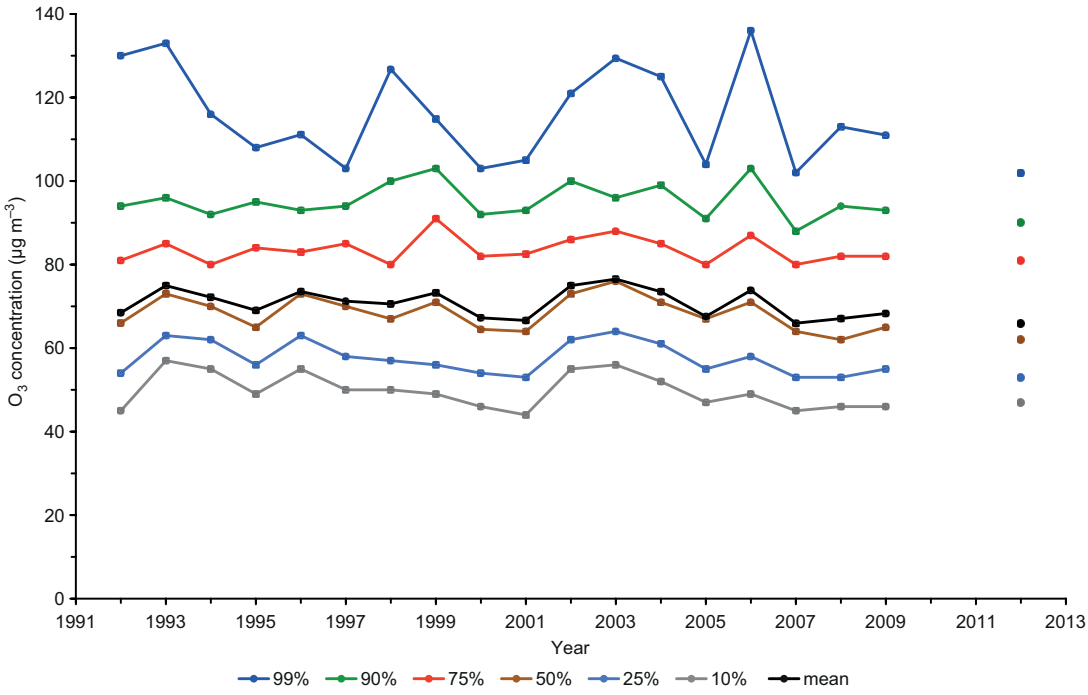

Fig. 3. Key percentiles and mean O_3 concentrations at Pallas in April–September from 1992–2012. The data for 2010–2011 are missing due to technical problems.

varied within the range 62–76 μg m^{-3}. The mean concentrations were close to the corresponding medians, as the frequency distribution of [O_3] at Pallas is approximately Gaussian. The highest concentrations, as indicated by the 99th percentile, exceeded 100 μg m^{-3} during each measurement year. These annual peak values were more variable than the lower percentiles, but did not progress towards lower or higher values, which is true for all the percentiles (*see* Fig. 3).

In addition to the concentration statistics, we present ozone concentrations in terms of the AOT40 index. AOT40 (expressed as μg m^{-3} h) is defined in an EU air quality directive (EU 2008) as the sum of the positive differences between the hourly mean concentration and a threshold of 80 μg m^{-3} (= 40 parts per billion), multiplied by the 1-h averaging time. The summation was carried out over May–July for a daily period of 8.00–20.00 UTC+1. EU (2008) lays down a target value of 18 000 μg m^{-3} h (averaged over five years) for the protection of vegetation. This value was not exceeded at Pallas in 1992–2012 (2010–2011 missing) (Fig. 4). A corresponding AOT40 value of 6000 μg m^{-3} h is set as an objective to be attained in the long term. This exposure level was exceeded during five years.

In addition to the standard definition with a 12-h daytime exposure window, the AOT40 was also calculated for the 24-h daily exposure period (*see* Fig. 4). Even though the concentrations were, on average, lower during the night half of the day, values greater than 80 μg m^{-3} were frequent and boosted the 24-h AOT40 to a significantly higher level than the 12-h AOT40. Independent of the accumulation period, the year-to-year variability of AOT40 was much larger than that of mean [O_3]. This is an inherent property of AOT40 and other threshold-based indices (Sofiev and Tuovinen 2001).

Trends

The trend in the time series of the bulk deposition and air quality measured at Pallas did not always remain constant during the whole monitoring period from 1992–2012 (Tables 2

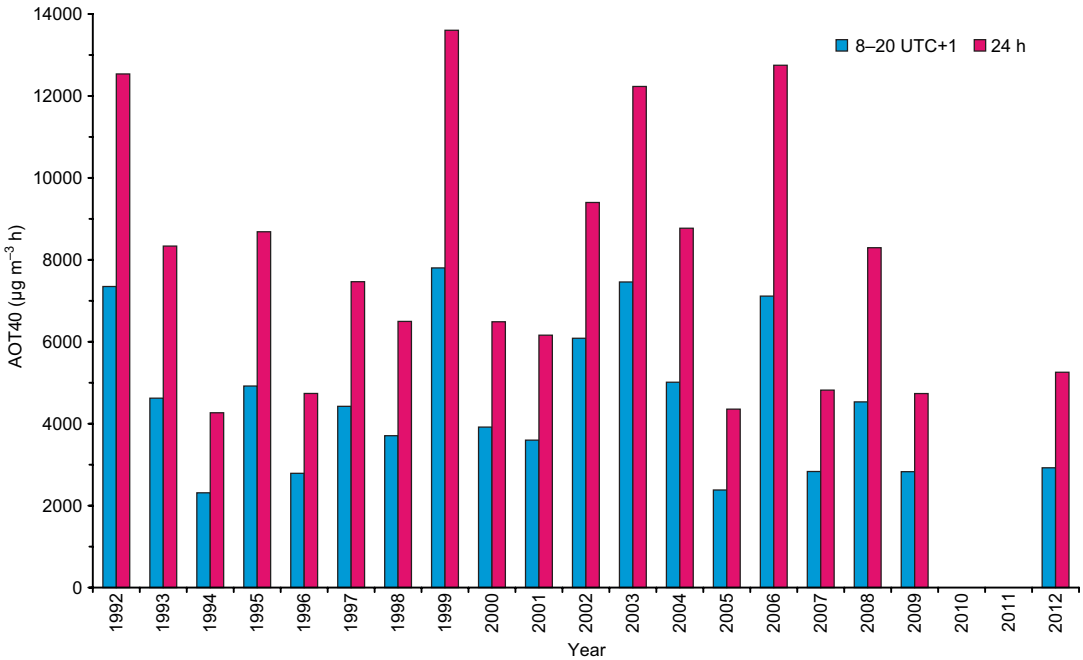

Fig. 4. Values of the AOT40 exposure index summed over May–July for 12-h (8:00–20:00 UTC+1) and 24-h daily periods. The data for 2010–2011 are missing due to technical problems. The other AOT40 values are scaled for missing data. The data coverage was typically higher than 90% (72% in 1997).

and 3). Therefore, significant turning points in the development of the monthly time series were determined with the help of a Gaussian low-pass filter, which filters out the short-term oscillations of the time series. Because air quality data are strongly affected by climatological factors, we feel that this method developed for climatological time series is also useful for the interpretation of air quality data. This moving and weighted average method was only used for visualization of the time series. Periods with a continuous trend of at least five years were sought. Because the ITSM time series analysis used for the calculations of the trends can handle the seasonality in the data, the calculations were applied to monthly bulk deposition. The greater number of data points per year also enabled the analysis of shorter time series with a constant development.

Both increasing and decreasing significant trends were found for the components related to the acidification and eutrophication of ecosystems, H^+, SO_4, NO_3 and NH_4 (Table 4). The periods for the trends differed between the components. The bulk depositions of NO_3 and NH_4 decreased for about five years starting in 1991. The annual change was 7% and 12%, respectively. Then, from early 1997, the NO_3 bulk deposition turned to an increase that continued for 191 months, until the end of the monitoring period discussed in this paper. The annual change was 3%. In the NH_4 time series, a period of a strong increase starting in the early 2000s and lasting for about five years was found. The SO_4 bulk deposition significantly decreased between 2005 and 2010. The hydrogen ion bulk deposition increased between 1997 and 2005.

The bulk deposition of the compounds connected to sea salt, Cl and Na, declined between 1991 and 2001 or 2002, Cl by 5% and Na by 7% annually. The bulk deposition of K decreased from the beginning of the monitoring period until the middle of 2003, whereas the bulk deposition of the other base cation, Ca, strongly increased between 1996 and 2002. Later, Ca bulk deposition declined. Finally, the Mg bulk deposition increased for about ten years starting in 1997.

The annual precipitation amount significantly increased by 2.9 ± 1.2 mm. This continuous time series was measured at the Alamuonio meteoro-

logical station, 23 km to the west of the Pallas IM station.

For the gaseous and particulate compounds in air, only a few significant trends for a period of at least five years were detected (Table 5). The sulphur compounds, SO_2 and particulate SO_4, declined annually by 3%–5% for 11 years starting in 1996. The trend calculation was not extended over the change in measuring method in 2007. For the nitrogen compounds, a significant trend was detected for NO_2 only. The five-year increase turned to a decrease in 2005.

Source areas

There was a considerable year-to-year variation in the source areas of SO_2 and NO_2 detected at Pallas. This can be due to variable meteorological conditions, which can, for instance, enhance gas-to-particle transformation and deposition, or varying industrial or residential emissions. However, some compound-specific (SO_2 and NO_2) general patterns could be observed (Fig. 5). For SO_2, the source area calculations were performed using the data from the SO_2 monitor at Sammaltunturi with a continuous time series.

Discussion

Sulphur compounds (SO_2, particulate SO_4, SO_4 bulk deposition)

The order of magnitude of the annual sulphate bulk deposition at Pallas was around 100 mg S m^{-2}. The critical load for acidification, based on EMEP dispersion modelling and the CCE database, was not exceeded in 2000 or beyond, whereas in 1990 a slight exceedance might have occurred (Hettelingh *et al*. 2012). Pallas is located far from the main European emission sources,

Table 4. Results of trend analysis based on the GLS-ARMA method for bulk deposition. Only statistically significant trends ($p < 0.05$) in the time series are shown. Intercept and slope in mg m^{-2} and mg m^{-2} $month^{-1}$, respectively, except for H^+ whose intercept and slope are expressed in mmol m^{-2} and mmol m^{-2} $month^{-1}$, respectively. Standard errors in parentheses. Annual change in % ± 95% confidence limits.

Component	Start	End	Months	Intercept	Slope	Change
H^+	Feb. 1997	Dec. 2005	107	427 (101)	4.7 (1.6)	13.1 (9.0)
SO_4-S	May 2005	Jul. 2010	63	10.8 (0.3)	–0.07 (0.01)	–8.4 (1.8)
NO_3-N	Nov. 1991	Jan. 1997	63	6.3 (0.3)	–0.04 (0.01)	–7.3 (3.1)
NO_3-N	Feb. 1997	Dec. 2012	191	4.5 (0.5)	0.01 (0.004)	3.3 (2.2)
NH_4-N	Nov. 1991	Aug. 1996	58	4.4 (0.4)	–0.04 (0.01)	–12.1 (7.4)
NH_4-N	Sep. 2001	Jan. 2006	68	1.8 (0.4)	0.06 (0.01)	38.5 (18.3)
Cl	Nov. 1991	Sep. 2002	131	11.0 (1.0)	–0.04 (0.01)	–4.9 (2.9)
Na	Nov. 1991	Aug. 2001	118	7.9 (0.7)	–0.05 (0.01)	–7.1 (3.0)
K	Nov. 1991	Jun. 2003	140	5.9 (0.5)	–0.04 (0.01)	–7.4 (2.5)
Ca	May 1996	Jan. 2002	69	0.9 (0.2)	0.03 (0.01)	40.0 (13.6)
Ca	Feb. 2002	Oct. 2008	81	2.7 (0.2)	–0.02 (0.01)	–8.1 (4.6)
Mg	Mar. 1997	Aug. 2006	114	0.45 (0.04)	0.003 (0.001)	6.9 (3.3)

Table 5. Results of trend analysis based on the GLS-ARMA method for the air compounds at Pallas. Only statistically significant trends ($p < 0.05$) in the time series are shown. Intercept and slope with standard errors in parentheses. Annual change in % ± 95% confidence limits.

Component	Start	End	Months	Intercept ($\mu g\ m^{-3}$)	Slope ($\mu g\ m^{-3}\ month^{-1}$)	Change (% $year^{-1}$)
SO_2	Jan. 1996	Dec. 2006	132	0.42 (0.05)	–0.002 (0.001)	–5.1 (3.9)
SO_4	Jan. 1996	Dec. 2006	132	0.39 (0.04)	–0.001 (0.001)	–3.3 (3.0)
NO_2	Aug. 1999	Apr. 2005	69	0.19 (0.03)	0.002 (0.001)	12 (10)
NO_2	May 2005	Aug. 2010	64	0.33 (0.03)	–0.003 (0.001)	–9.2 (5.7)

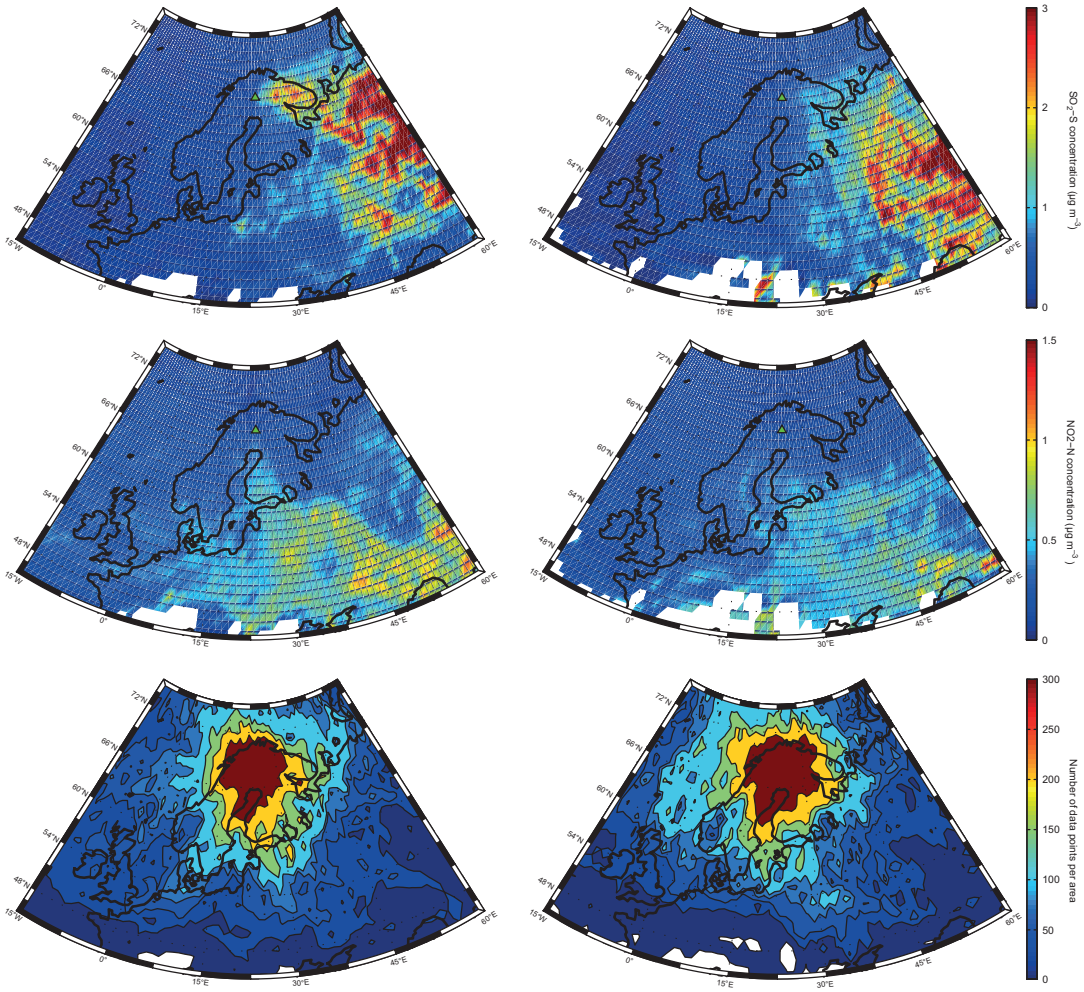

Fig. 5. Source areas of SO_2 (top row) and NO_2 (middle row) detected at Pallas in 2001 (left column) and 2010 (right column). In the bottom row, the heat maps for each year are presented.

and the level of the sulphur bulk deposition is consequently lower than at the other Finnish IM stations (Vuorenmaa *et al*. 2013). At the northernmost subarctic Swedish station, Myrberg, with bulk deposition measurements from an open area, the mean annual sulphur bulk deposition was also about 100 mg S m^{-2} between 1990 and 2011 (Pihl Karlsson *et al*. 2012a). The monitoring result for the sulphur bulk deposition at Pallas is also consistent with recent estimates using the Hilatar chemistry transport model with elaborated emissions for the Kola Peninsula and an accurate ship emission inventory (Hongisto 2014).

The bulk deposition of sulphur at Pallas decreased by 17% from the beginning of the 1990s to the beginning of the 2000s (Table 2), whereas during the second half of the monitoring period, bulk deposition slightly increased. Between 2005 and 2010, a significant trend of 8% annual decline was detected in the time series (Table 4). This decrease is consistent with trends observed at the other IM stations (Vuorenmaa *et al*. 2013).

In the input–output budgets studied in the Integrated Monitoring programme, the key factor is the deposition of compounds related to acidification and eutrophication of ecosystems. Therefore, the development of deposition is the main focus in this paper. However, the variable precipitation amount might mask interesting develop-

ments in the concentration of the compounds in precipitation. In the Pallas area, the annual mean concentrations of sulphate, nitrate and ammonium in precipitation behaved different between 1992 and 2012 (Fig. 2A). Sulphate concentrations decreased. The precipitation amount in 1992–2012 annually increased by 0.6%, which at least partly counteracted the effect of the decreasing SO_4 concentration in precipitation during the last ten years of the monitoring. The effect of the decreasing emission did not show in the ammonium and nitrate concentrations. The time series of the annual volume-weighted concentration shows that the development in the concentration of these compounds is not directly linked to the annual precipitation amount (*see* Fig. 2A).

The sampling method for determining the air concentrations of sulphur and nitrogen compounds changed in 2007, which started a new time series not comparable to the older one. Thus, the trend calculations for these cover the period until the end of 2006. The SO_2 and particulate SO_4 concentrations decreased in 1992–2006 by 5% and 3% annually, respectively. The large decline in sulphur emissions (data from the EMEP database http://www.ceip.at/webdab-emission-database) in areas contributing 60% to the Finnish sulphur deposition, i.e. Finland, Russia (especially the Kola Peninsula and St. Petersburg area), Poland, Estonia and Ukraine (Gauss *et al*. 2013), is reflected in the Pallas results during the first half of the monitoring. However, the sulphur concentration and deposition results at Pallas did not fully follow the 30%–50% emission decrease in the same source areas in the 2000s. This might have resulted from the increased precipitation amount, but also from uncertainties in the emission estimates. The deficiency of emission information for the Kola Peninsula has been noted in recent simulations (Prank *et al*. 2010, Hongisto 2014).

The source area analysis was performed using the SO_2 hourly data measured at Sammaltunturi and not the daily filter pack SO_2 results at Matorova discussed above. Notably, the annual mean values of SO_2 measured with the continuous monitor at Sammaltunturi were higher than the values measured with the filter pack method at Matorova. According to a comparison between these two methods, the correlation between the daily mean values of seven years at Oulanka subarctic station was good (r^2 = 0.99), but the monitor produced 16% higher values than the filter method (Leppänen *et al*. 2005). The difference was partly explained by low values near the detection limit of the methods, which are 0.04 μgS m^{-3} for the filter pack and 0.13 μg S m^{-3} for the monitor. Moreover, the hourly data were given for standard conditions (20 °C, 1 atm pressure), whereas the filter pack results were recorded in changing ambient conditions (Leppänen *et al*. 2005). We expect that the parallel use of data from these two methods will not cause confusion in this paper, because the monitoring data are only used in the source area analysis with a focus on the relative difference between the emission areas, and the correlation between the results of the methods is good.

In 2001 and 2010, the annual means of SO_2-S at Sammaltunturi in Pallas were 0.56 and 0.44 μg m^{-3}, respectively, so the latter was slightly lower. In both years, as well as in all years in the source area study, the highest concentrations of SO_2 were found in the continental air masses originating in northwestern Russia (Fig. 5). However, in 2010, the air masses from the Kola Peninsula had lower concentrations of SO_2 than in 2001, which may be one reason for the lower annual mean value. From the heat maps, we can see that the Kola Peninsula was an equally important source area in terms of air mass frequencies during both years.

Nitrogen compounds (NO_2, gaseous and particulate HNO_3 + NO_3, NO_3 bulk deposition, gaseous and particulate NH_3 + NH_4 and NH_4 bulk deposition)

The annual bulk depositions of nitrogen and ammonium at Pallas were under 100 mg N m^{-2} and around 50 mg N m^{-2}, respectively. The NO_2 concentration in air was around 0.3 μg N m^{-3}. Similar values were measured at the subarctic Myrberg station in Sweden (Pihl Karlsson *et al*. 2012a). As compared with that at all the other IM stations in the network, the level of the total inorganic nitrogen bulk deposition from bulk

samplers was lowest at Pallas (Vuorenmaa *et al*. 2013).

The levels of the gaseous and particulate nitrate and ammonium at Pallas during the monitoring period were constantly low, around 0.05 and 0.10 μg N m^{-3}, respectively. Within the NitroEurope project, monthly concentrations of gaseous and aerosol nitrogen compounds were also measured with denuders at Matorova in Pallas during 2007–2008. With this method, the mean values for the atmospheric nitrate and ammonium compounds were 0.05 and 0.30 μg N m^{-3}, respectively (Flechard *et al*. 2011). The correspondence between the time series was extremely good for the nitrate concentration and satisfactory for the ammonium concentration, taking into account that the values measured were near the detection limits of both of the measurement methods.

The main objective of the NitroEurope project was to estimate the dry deposition fluxes of reactive nitrogen to European ecosystems. This part of the nitrogen deposition could not be estimated from our Pallas monitoring data, which makes the results of the NitroEurope project especially valuable in the IM context. For the Pallas site, the annual median value of the dry deposition calculated with four different models was 30 mg N m^{-2}, from which the ammonia + ammonium dry deposition was more than half. At the other Finnish subarctic NitroEurope site in Sodankylä, the dry deposition flux was 130 mg N m^{-2} (Flechard *et al*. 2011). In northern Sweden, the relative share of dry deposition from the total inorganic nitrogen was estimated at less than 8% according to measurements with a special device for dry deposition (Pihl Karlsson *et al*. 2012b). Calculated from our results and the NitroEurope the dry deposition estimate, the share of dry deposition at Pallas is greater than in the Swedish study.

The share of organic nitrogen deposition was not covered by the monitoring at Pallas. The bioavailability of organic nitrogen is not well known. In a recent review, Cornell (2011) estimated the share of the organic nitrogen to be in the range of 10%–25% of the total nitrogen deposition.

In our measurements at Pallas, the bulk deposition of nitrate decreased annually by 7% between 1991 and 1997. After 1997, it increased by 3% until the end of the monitoring period. Likewise, the ammonium bulk deposition first decreased, but then strongly increased during a 6-year period from 2001 to 2006. No large change was measured in the sum of the gaseous and particulate nitrate or ammonium. For the NO_2 concentration, the results since 1999 were available. During the first five-year period, the concentration increased and then turned to a decline for another five-year period.

At Pallas, the nitrate bulk deposition covered about 70% of the sum of the inorganic bulk deposition. This sum of the nitrate and ammonium deposition increased similarly to the nitrate bulk deposition: the annual change in the sum was +2.5% between 1997 and 2012. Thus, the ecosystems have received increasing amounts of deposited nitrogen since the mid-1990s. However, the critical load for eutrophication, based on EMEP dispersion modelling and the CCE database, was not exceeded at Pallas during the period of the monitoring (Hettelingh *et al*. 2012).

For the terrestrial ecosystems, the observation of an increase in the nitrate bulk deposition is notable. In order to estimate the extent of this development, the monitoring results of the other Finnish subarctic stations were examined. The NO_3 bulk deposition followed a decreasing trend at the Finnish stations until it turned to an increase at the end of the 2000s (Fig. 6).

The increase in the nitrate bulk deposition was confirmed by the trend calculations. The nitrate bulk deposition increased at all Finnish subarctic stations except Oulanka, where no significant trend was detected after 2003 (Table 6). At Kevo and Sodankylä, the change per year was larger than at Pallas, but the period with a significant trend was shorter. No significant change in the bulk deposition of inorganic nitrogen was detected at the Swedish subarctic stations between 1997 and 2008 (Pihl Karlsson *et al*. 2011), whereas at Hundshögen, a high-level station (1250 m a.s.l.) in central Sweden, the bulk depositions of both nitrate and ammonium increased during 2000–2010 (Pihl Karlsson *et al*. 2012b). Fowler *et al*. (2007) reported an increase in the concentration of NO_3 in precipitation in remote areas of Europe during 1980–2000, typically by 50%. The increase might be important

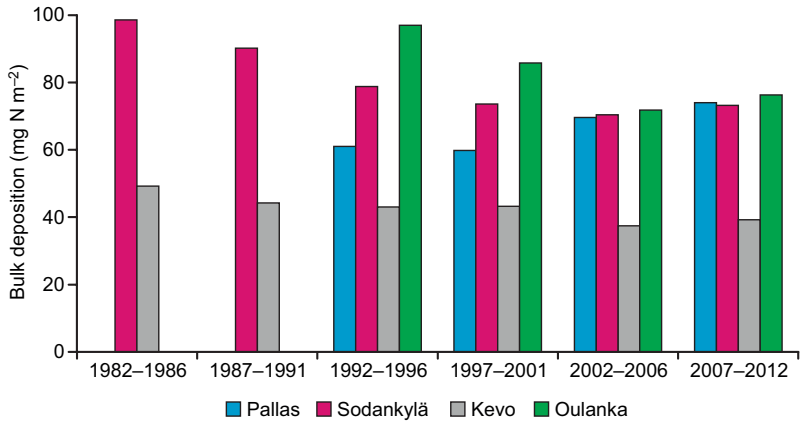

Fig. 6. Five-year mean bulk deposition of NO_3-N at the Finnish subarctic stations. The last period covers six years.

for plant species adapted to a very limited atmospheric nitrogen supply. An increase in the nitrate bulk deposition was also detected at the Finnish Valkea-Kotinen IM station between 2002 and 2008 (Ruoho-Airola *et al*. 2014).

The monitoring result for the bulk deposition of the nitrogen compounds at Pallas is consistent with the recent estimates using the Hilatar chemistry transport model with elaborated emissions for the Kola Peninsula and an accurate ship emission inventory (Hongisto 2014). The share of the Baltic Sea shipping traffic was in the order of 5% at Pallas for nitrate deposition (Hongisto 2014). The Arctic shipping lines pass rather close to the Pallas area, and the NO_x emissions from these are projected to significantly increase, as declining sea ice cover is likely to expand shipping operations in the Arctic Basin (Corbett *et al*. 2010). As a result of this expansion, a deposition increment of up to 30 mg N m^{-2} in northernmost Europe has been estimated (Tuovinen *et al*. 2013). An additional nitrogen load exceeding this is possible if maritime emissions within the area are further increased by the diversion of global traffic through emerging Arctic routes.

The development of the nitrogen compounds in Pallas did not clearly reflect the reported emission reductions. The areas contributing around 70% to the Finnish nitrogen deposition are Russia (especially the Kola Peninsula and St. Petersburg), Finland, Germany and Poland for both nitrogen components, as well as the Baltic Sea and North Sea ship traffic for NO_x deposition and Belarussia and Sweden for the NH_y deposition (Gauss *et al*. 2013). The sum of NO_x emissions from these source areas declined by 20% in the 1990s according to the EMEP emission database, while the reduction in NH_y emissions was 15% (http://www.ceip.at/webdab-emission-database). In the 2000s, NO_x emissions declined by about 10% and NH_y emissions by only 5%. The emission estimates used for the EMEP model calculations include both increasing and decreasing development in the nitrogen

Table 6. Results of trend analysis based on the GLS-ARMA method for the NO_3-N bulk deposition time series at Finnish subarctic stations. Only statistically significant trends ($p < 0.05$) in the time series are shown. Intercept and slope with standard errors in parentheses.

Station	Start	End	Months	Intercept (mg m^{-2})	Slope (mg m^{-2} month^{-1})	Change (95%CI) (% year^{-1})
Kevo	Nov. 1991	Aug. 1996	58	4.3 (0.2)	–0.03 (0.01)	–7.0 (3.5)
Kevo	Feb. 1999	Aug. 2003	55	4.2 (0.4)	–0.03 (0.01)	–9.4 (7.7)
Kevo	Jan. 2009	Jun. 2012	42	2.6 (0.4)	0.04 (0.02)	19.0 (16.0)
Sodankylä	Nov. 1991	Jun. 1997	68	7.9 (0.3)	–0.04 (0.01)	–6.6 (2.8)
Sodankylä	Jan. 2006	Dec. 2012	84	4.7 (0.2)	0.03 (0.00)	7.6 (2.4)
Oulanka	Nov. 1991	Oct. 2003	114	9.4 (0.6)	–0.03 (0.01)	–3.7 (1.9)

compounds on the Kola Peninsula after 1997. Presumably, the small but continuous increase in the nitrate bulk deposition at Pallas is partly a consequence of the changes in emissions from the Kola Peninsula. The remarks about the uncertainties of the emissions from the Kola Peninsula discussed earlier in connection with the sulphur compounds are also valid for the NO_x emissions.

In 2001 and 2010, the annual means of NO_2-N at Pallas were 0.22 and 0.19 μg m^{-3}, respectively. As compared with the SO_2 source areas, the NO_2 source areas are more diffuse and more southwestern (Fig. 5). This could be due to the highly diffuse traffic emissions originating from the densely populated areas. Unlike SO_2, southern Finland also emerges as a source area for NO_2.

Ozone

The statistics for ozone concentrations at Pallas (Fig. 3) show characteristics of an environment that is located in the northern latitudes but south of the pristine Arctic, with a discernable anthropogenic influence. Tropospheric ozone largely originates from *in situ* photochemical reactions involving precursor compounds of both anthropogenic and biogenic origin. In remote and rural areas, ozone production is controlled by the presence of nitrogen oxides (NO_x = NO + NO_2), which catalyse the oxidation of volatile organic compounds (VOCs), methane and carbon monoxide. In the subarctic region, the pronounced seasonal cycle of solar radiation exerts a strong controlling influence on the chemical reactions that drive ozone production and destruction. The annual [O_3] cycle at Pallas shows a spring maximum, which is typical of remote northerly sites in Europe. For further discussion, *see* Laurila (1999), Hatakka *et al*. (2003) and Laurila *et al*. (2009).

In addition to photochemistry, the diurnal [O_3] cycle is strongly influenced by the dynamics of vertical mixing of the troposphere and deposition on vegetation and other surfaces. As the ozone data of Pallas originate from the top of a mountain, about 300 m above the surrounding terrain, the diurnal variation in [O_3] is very limited (Hatakka *et al*. 2003). Rather, the concentration variations are predominantly related to the origin of air masses, with the lowest [O_3] during the summer half of year, typically being observed when Arctic air enters the site. The highest concentrations most often occur in southern air masses and can thus be attributed to ozone production from European precursor emissions (Laurila *et al*. 2009).

Owing to the key role of meteorological conditions in [O_3] variability (Jonson *et al*. 2006), the year-to-year fluctuations are much greater within the highest concentration percentiles that reflect specific pollution episodes, as compared with the low percentiles that are more associated with the hemispheric background concentrations. While there is an indication that the peak concentrations have declined in some regions of Europe, in accordance with the NO_x and VOC emission reductions achieved as a result of the air pollution abatement measures undertaken in Europe during the last decades (Tørseth *et al*. 2012), no such development can yet be observed at Pallas.

The AOT40 index, which is included in the EU air quality directive (EU 2008), reflects the risk of detrimental effects on vegetation due to tropospheric ozone. While the target value of EU legislation was not exceeded at Pallas during the study period, the corresponding long-term objective was not attained. According to the EU definition, the AOT40 is to be calculated over a fixed period from 8.00–20.00 UTC+1, based on the rationale that these hours correspond to the period of active gas exchange of plants. As Pallas is located in the subarctic region, this time window may be too restrictive relative to the actual daylight period. The AOT40 calculated without a daytime condition shows the potential for much higher vegetation exposure to harmful ozone levels (Fig. 4).

It is important to note that the AOT40 index is based on ambient concentrations only, while the plant physiological effects depend on ozone uptake via stomata. Thus, a more advanced risk indicator that accumulates the dose actually absorbed by vegetation has been adopted in the current risk assessment methodology of the CLRTAP (UNECE 2010). The application of such a dose-based indicator suggests that the risk

predicted in this way is regionally more widespread than that based on the AOT40 (Simpson *et al*. 2007). Recent model calculations by Tuovinen *et al*. (2013) show that the critical ozone dose, above which significant biomass loss may occur, is also exceeded for forest trees in northernmost Europe, except for a limited area northwest of Pallas. These calculations also suggest that climate warming may enhance stomatal ozone uptake in northern Europe, and thus increase exceedance of the critical level.

Chloride and the base cations

The bulk depositions of chloride and sodium decreased by around 40% between 1992–1994 and 2001–2003 (Table 2). In the same period, the bulk deposition of potassium decreased by 73%, and that of calcium and magnesium increased by 47% and 21%, respectively. During the second half of the monitoring period, most bulk depositions increased, but the changes were smaller than at the beginning of the period.

Sodium and chloride in precipitation are mainly derived from sea salt spray, and the variations in their depositions are driven by meteorological factors. At the Alamuonio meteorological station, the proportion of northern winds was at the same level, about 10%, during 1992–2012. However, the mean wind speed of the northern winds was 40% higher in 1992–1994 than 2010–2012, which might explain the higher bulk depositions of Cl and Na (Table 2), which largely originate from the North Sea and the Arctic Sea.

Contrary to the general declining trend in Europe, the calcium bulk deposition increased between 1996 and 2002 (Table 2) (Tørseth *et al*. 2012). This might be connected with the change in the measuring site in 2000 from Särkijärvi to Matorova. Calcium is largely derived from soils, which differ between these sites. The open field at Särkijärvi was probably the source of the increasing Ca bulk deposition. Therefore, the two time series of calcium bulk depositions are not comparable. For other compounds, except possibly K, no sudden change in the concentrations or bulk depositions was detected. The Ca bulk deposition at the Matorova site after 2000 followed the general decreasing Ca development (Tørseth *et al*. 2012).

The high average annual bulk deposition of potassium in 1992–1994 is due to three large monthly values, each comparable to the annual mean in 2001–2003. These samples may have been contaminated by biological material, which makes even the average value uncertain. However, the trend calculation is not affected by single uncertain monthly values. Instead, the change in the measuring site from Särkijärvi to Matorova might have influenced the K bulk deposition due to the different type of vegetation in the surroundings of the sampler. The variation in the time series decreased after 2000.

The annual bulk depositions of Ca and Mg at Pallas in 2010 were at the same level as those reported for the Swedish subarctic station Myrberg (Hansen *et al*. 2013). For other base cations than K, the EMEP estimates were higher (Hansen *et al*. 2013).

Conclusions

The N cycle in the environment has attracted increasing interest in recent years, one reason for this being the slower decline in N emissions than in S emissions. At Pallas, the level of nitrogen deposition was low as compared with that at the other Finnish IM stations, but it has been increasing since the mid-1990s. The present level of the atmospheric nitrogen deposition does not pose any direct hazard to terrestrial ecosystems; it could even increase forest growth, but excessive nutrient inputs may disturb the balance of the vulnerable arctic ecosystems. The NO_x emissions from expanding shipping activities in the Arctic region may significantly enhance the nitrogen load to these ecosystems. They are also likely to increase the ozone stress on vegetation, which is already close to or slightly above the critical level.

Environmental changes due to climate change are estimated to take place earlier and to be stronger in the Arctic. Changes in the climate might also alter the transport routes for air pollutants. Thus, the monitoring results of the Pallas subarctic IM station could be used to provide an early warning of the threats for the ecosystems.

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